Local structure of Iridium organometallic catalysts covalently bonded to carbon nanotubes.

2016 J. Phys.: Conf. Ser. 712 012052

(http://iopscience.iop.org/1742-6596/712/1/012052)

Local structure of Iridium organometallic catalysts covalently bonded to carbon nanotubes.

J Blasco[1], V Cuartero[2], G Subías[1], M V Jiménez[3], J J Pérez-Torrente[3], L A Oro[3], M Blanco[4], P Álvarez[4], C Blanco[4] and R Menéndez[4]

[1]Instituto de Ciencia de Materiales de Aragón, Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza (Spain)
[2]ESRF-The European Synchrotron, 71, Avenue des Martyrs, Grenoble (France)
[3]Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea-ISQCH, Universidad de Zaragoza-CSIC, C/ Pedro Cerbuna 12, 50009 Zaragoza (Spain)
[4]Instituto Nacional del Carbón, CSIC, P.O. Box 73, 33080 Oviedo (Spain)

E-mail: jbc@unizar.es

Abstract. Hybrid catalysts based on Iridium N-heterocyclic carbenes anchored to carbon nanotubes (CNT) have been studied by XAFS spectroscopy. Oxidation of CNT yields a large amount of functional groups, mainly hydroxyl groups at the walls and carboxylic groups at the tips, defects and edges. Different kinds of esterification reactions were performed to functionalize oxidized CNT with imidazolium salts. Then, the resulting products were reacted with an Ir organometallic compound to form hybrid catalysts efficient in hydrogen transfer processes. XANES spectroscopy agree with the presence of Ir(I) in these catalysts and the EXAFS spectra detected differences in the local structure of Ir atoms between the initial Ir organometallic compound and the Ir complexes anchored to the CNT. Our results confirm that the halide atom, present in the Ir precursor, was replaced by oxygen from –OH groups at the CNT wall in the first coordination shell of Ir. The lability of this group accounts for the good recyclability and the good efficiency shown by these hybrid catalysts.

1. Introduction

Carbon nanotubes (CNT) can be considered as a versatile matrix to develop heterogeneous catalysts with improved activity [1]. Here we report a thorough characterization by X-ray absorption fine structure spectroscopy (XAFS) of a set of catalysts based on N-heterocyclic carbene (NHC) iridium complexes covalently bonded to CNT properly functionalized with imidazolium salts. These materials showed catalytic activity in hydrogen transfer processes and they were tested in the hydrogenation of cyclohexanone with 2 propanol showing both good efficiency and good recyclability [2].

Chemical oxidation of CNT yields different oxo-groups that can be functionalized. Hydroxyl groups are located at the basal planes of CNT walls whereas carboxylic acids mainly lie at the tips, edges and defects of CNT (see Fig. 1a). These oxidized CNT materials can react directly with some methoxo-cylooctadiene iridium dimer complexes, $[\{Ir(\mu\text{-}OMe)(cod)\}_2]$ (cod=1,5-cyclooctadiene), resulting poor catalytic activity [2]. Better results were obtained when oxidized CNT were functionalized with the imidazolium salts (Im) like $[MeImH(CH_2)_3OH]Cl$ (chloride of 3-methyl-1-(3-hydroxypropil)-

imidazolium, hereafter denoted as Im-1) or [MeImH(1-cyclohexyl-2-ol]I (iodide of 3-methyl-1-(1-cyclohexyl-2-ol)-imidazolium (denoted as Im-2) rendering functionalized *f*-CNT supports for NHC iridium complexes synthesis by simple reaction with [{Ir(μ-OMe)(cod)}$_2$]. Two ways to functionalize CNT were tested, either esterification reactions of –COOH groups with Im-1 or Im-2 (denoted as CNT-1 and CNT-2, respectively) and activation of –OH groups with *p*-nitrophenylchloroformate followed by the reaction with Im-1 (denoted as CNT-pNPh-1). Both functionalized CNT were then reacted with [{Ir(μ-OMe)(cod)}$_2$] to yield the hybrid catalysts: CNT-1-Ir, CNT-2-Ir and CNT-pNPh-1-Ir. In the latter case, the Ir complex can be also anchored to the reactive –COOH groups. In order to discriminate activities obtained from those different anchoring points, some CNT were thermally reduced at 400ºC in inert atmosphere to remove –COOH groups. The resulting product was functionalized in the same way as CNT-pNPh-1-Ir and then reacted with the Ir precursor, resulting in a supported NHC complex without secondary products, which was named CNT-T400-pNPh-1-Ir. Figures 1b-e show the proposed final structure for the hybrid catalysts synthesized.
The local iridium structure is unknown but the halide ligand is proposed to remain in the first coordination shell of the Ir atom and the output release of this anion from the coordination sphere of the metal is suggested as the initiation of the catalysis mechanism [2]. In order to examine this possibility, XAFS spectroscopy has been used with the aim of studying both the electronic state of Ir atoms and its local environment in these hybrid catalysts.

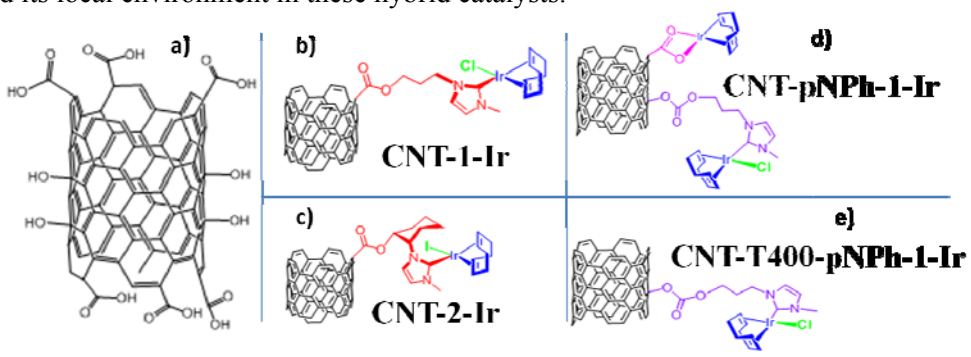

***Figure 1**. (a) Oxidized CNT and (b-e) presumed structures for the hybrid catalysts.*

2. Experimental section.

XAFS spectra at the Ir L_3-edge were recorded at the BL22-Claess (Alba) and at the BM23 (ESRF) beamlines on fresh samples. The measurements were carried out in transmission mode at room temperature on pellets of the materials mixed with cellulose if necessary. The beam was monochromatized by a fixed-exit Si (111) double crystal and harmonic rejection better than 10^{-5} was achieved by using the Si mirror coating of the double flat mirror installed after the monochromator. Energy resolution was estimated to be ~8×10^{-5} at the Ir L_3-edge and a pellet of Ir metal with cellulose was simultaneously measured for energy calibration. The XANES spectra were normalized at ~100 eV beyond the absorption edge. We have also recorded spectra of Ir-metal and IrCl(cod)[MeIm$(CH_2)_3$OH] as references for Ir^0 and Ir^+ respectively. The second compound is labelled as Ir(I)-reference and its structure can be seen in the inset of the figure 2a.
EXAFS signal extraction and background removal were carried out using Athena software [3] and the EXAFS structural analysis was performed using the ARTEMIS program [3] which makes use of theoretical scattering amplitudes and phases calculated from FEFF6 code [4] for the several single and multiple scattering paths. The fits were carried out in the R-space using a Hanning window in the region 1.1- 2.3 Å which only include contributions from the first coordination shell as it is correlated to the main differences in the local environment of Ir atoms.

3. Results and conclusions.

Figure 2a shows the derivative of the absorption coefficient vs energy about the Ir L_3-edge for representative catalysts compared to the ones for Ir^0 and the Ir(I)-reference. All catalysts exhibit the

first inflection point at the same energy that concurs with Ir(I)-reference suggesting a similar oxidation state for the Ir atoms at CNT-catalysts.

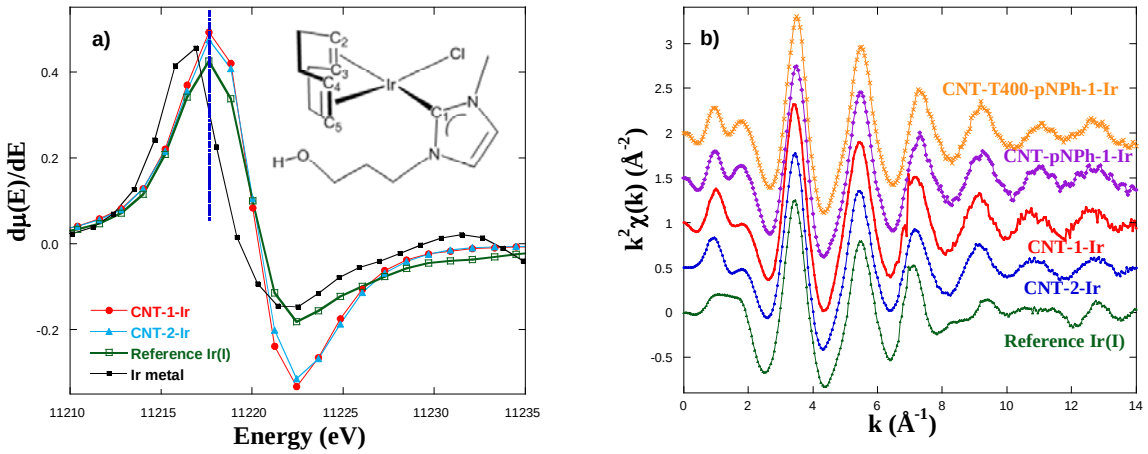

Figure 2. *(a)Derivative of the absorption coefficient vs. energy al the Ir L_3-edge for CNT-1-Ir, CNT-2-Ir, Ir(I)-reference and Ir^0. Vertical line shows the inflection point for the Ir(I) compounds. Inset: Structure of the Ir(I)-reference compound. (b) EXAFS spectra, $k^2 \times \chi(k)$, at the Ir L_3-edge for the indicated CNT-based catalysts and the Ir(I)-reference at room temperature.*

The extracted EXAFS signals at room temperature for all studied samples are compared in Figure 2b for the sake of comparison. CNT-based catalysts exhibit similar EXAFS oscillations but the Ir(I)-reference has noticeable differences in the $8Å^{-1} \leq k \leq 12Å^{-1}$ range. Figure 3a shows the Fourier transform (FT) of the k^2-weighted EXAFS spectra, calculated between 2.75 and 14 $Å^{-1}$ using a Hanning window. All CNT-based catalysts show a strong peak at 1.67 Å (without phase shift correction) corresponding to the first coordination shell. This distance agrees with the expected one for Ir-C bond length. The Ir(I)-reference shows the same peak but with less intensity which can be ascribed either to a higher disorder or fewer Ir-C paths respect to the Ir in hybrid catalysts. In addition, the FT of Ir(I)-reference displays a shoulder at ~2.0 Å ascribed to the Ir-Cl bond length that is lacked in the CNT-based catalysts.

The structural analysis was carried out as indicated in the experimental section. We have considered contributions from single scattering paths, Ir-C, Ir-O and Ir-Cl. The representative best fits for the Ir(I)-reference and a representative catalyst are shown in the figure 3b. The Ir(I)-reference was analyzed using the local environment indicated in the figure 2a and the fit agrees with a first coordination shell composed by 5 Ir-C paths and an additional Ir-Cl contribution with the following bond lengths: Ir-C_1= 2.03(1) Å, Ir-C_2(C_3)= 2.11(1) Å, Ir-C_4(C_5)= 2.19(1) Å and Ir-Cl= 2.43(1) Å in agreement with reported structural data in related compounds [5]. However, this environment failed to fit the EXAFS signal of CNT-based catalysts. Preliminary fits clearly showed the absence of Cl paths in the CNT-1-based catalysts (or I in the CNT-2-compound) as the resulting bond length was unphysical long and the fit was very poor. Hence, the logical hypothesis is that chloride (or iodide) has been displaced by another nucleophile and the most logical candidate was the –OH groups from the CNT wall. Therefore, we replaced the Ir-Cl path by an Ir-O one and the fit converged to yield an Ir-O distance similar to the previous Ir-C_1. Therefore, we performed the structural analysis using this model and some constrains were imposed to avoid over-parametrization. We only refined 5 parameters: an inner potential correction (ΔE_0), and average Debye-Waller factor (σ^2) and three distances R_1, R_2 and R_3 accounting for C_1+O, C_2+C_3 and C_4+C_5, respectively. The best fit parameters are summarized in the table 1 for the four catalysts. The amplitude reduction factor s_0^2 was set at 1.0, following the previous fit of the reference compound and in agreement with previous calculations [6]. The data from table 1 indicate a similar local environment for Ir atoms in all hybrid catalysts no matter the kind of

functionalization performed. In all cases, the first coordination sphere around Ir atoms is composed by six light elements (C and O) without sign of halides.

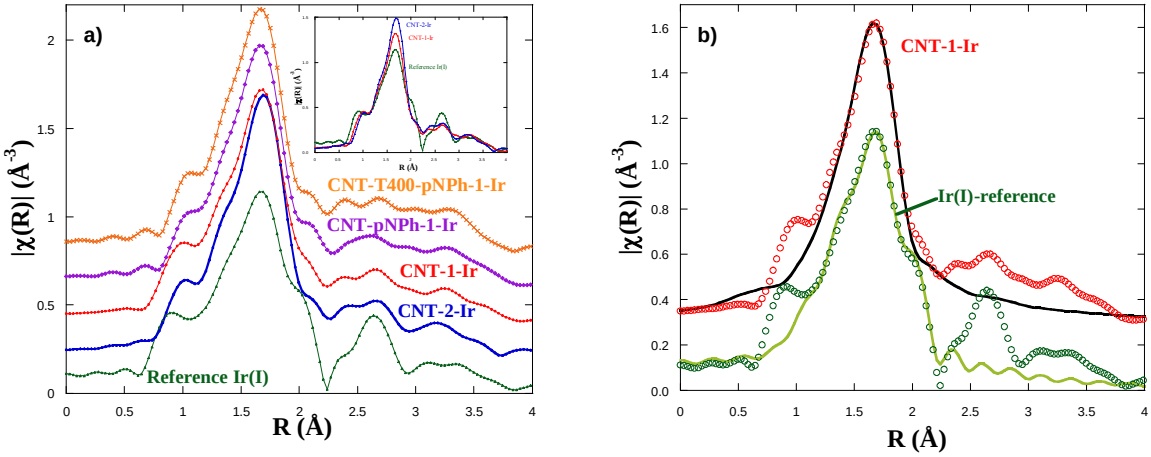

Figure 3. *(a) Modulus of the Fourier transforms (FT) extracted from the curves of Fig. 2b. Inset: Direct comparison of representative samples. (b) Comparison of the FT (circles) to the best fits (lines) for two representative samples. The fit was limited to the first coordination shell.*

Table 1. Best fit parameters (inner potential, bond lengths, average Debye-Waller factor and reliability factors [3]) obtained from the fitting of EXAFS data in the R-space mode. Numbers in parentheses refer to standard deviation of the last significant digits.

Sample	ΔE_0 *(eV)*	R_1*(Å)*	R_2*(Å)*	R_3*(Å)*	σ^2(Å^2) $\times 10^{-3}$	R_F
CNT-1-Ir	3.9(9)	2.035(19)	2.107(26)	2.186(24)	4.3(19)	0.0043
CNT-2-Ir	3.9(7)	2.029(21)	2.101(14)	2.186(20)	1.7(14)	0.0028
CNT-pNph-1-Ir	3.6(8)	2.029(21)	2.083(34)	2.172(32)	3.1(19)	0.0038
CNT-pNph-1-T400-Ir	3.3(9)	2.024(37)	2.090(28)	2.158(37)	2.9(22)	0.0049

Summarizing, XAFS spectroscopy resulted very useful to discern the local structure around Ir atoms in CNT-based hybrid catalysts. Halide ions (Cl in CNT-1 or I in CNT-2) are lost during the synthesis process to obtain the hybrid catalysts. They are likely replaced by –OH groups from the CNT wall. The lability of these –OH groups explains the good recyclability shown by these catalysts [2,7].

Acknowledgments.
Authors acknowledge the financial support from Mineco/FEDER CTQ2010-15221, MAT2012-38213-C02-01, and DGA E07 and E69 projects. They also thank Alba for granting beam time and the kind assistance of Claess staff. M. Blanco thanks MECD for his FPU grant (AP2010-0025).

References

[1] Schaetz A, Zeltner M and Stark W J 2012 *ACS Catal.* **2** 1267.
[2] Blanco M *et al.* 2013 *ACS Catal.* **3** 1307.
[3] Ravel B and Newville M 2005 *J. Synchrotron Radiat.* **12** 537.
[4] Rehr J J and Albers R C 2000 *Rev. Mod. Phys.* **72** 621.
[5] Jiménez M V *et al.* 2011 *Organometallics* **30** 5493.
[6] Roy M, Gurman S J and van Dorssen G 1997 *J. Phys. IV* **7** 151.
[7] Blanco M *et al.* 2016 *Carbon* **96** 66.